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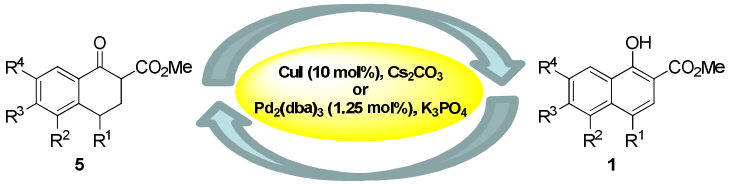
José F. Cívicos,[b] Carlos M. Rocha,[a,c] Paulo R. R. Costa,[b*] and Carmen Nájera[a]*



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Copper- *versus* palladium-catalyzed aromatization of 2-(methoxycarbonyl) tetralones: synthesis of methyl 1-hydroxy-2-naphthoates

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ABSTRACT

The aromatization of α-tetralones substituted at the β-position by an ester group is reported using either CuI or $Pd_2(dba)_3$. In the case of using CuI (10 mol%) as catalyst and Cs_2CO_3 as base in dioxane, 2-(methoxycarbonyl)-α-tetralones are smoothly converted into the corresponding methyl 1-hydroxy-2-naphthoates at 70 ºC under air. Alternatively, $Pd_2(dba)_3$ (1.25 mol%) can also be used as catalyst in the presence of K_3PO_4 as base in toluene also at 70 ºC under argon. These are the most straightforward methodologies for the aromatization of these types of α-tetralones. CuI is the catalyst of choice due to higher efficiency, economical and practical reasons.

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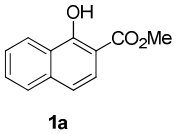
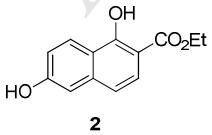
1. Introduction

Naphthol derivatives bearing an ester group at the β-position showed widely biological and medicinal properties. For instance, methyl 1-hydroxy-2-naphthoate (**1a**, MHNA)[1] and ethyl 1,6-dihydroxy-2-naphthoate (**2**)[2] have shown inflammatory properties and the corresponding tetrazole derivatives are potential antiallergy agents.[3] This 1-hydroxy-2-naphthoate unit is present in natural products such the cytotoxic compounds 3-hydroxymollugin (**3**) and 3-methoxymollugin (**4**).[4] In addition, these hydroxynaphthoates have been used as precursors for the synthesis of taiwanin C,[5] a epipodophyllotoxin analog,[6] α,β-sorigenin methyl ethers[7] and olivine trimethyl ether.[8]



1a



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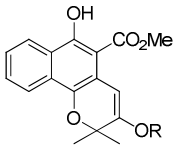


3: R = H
4: R = Me

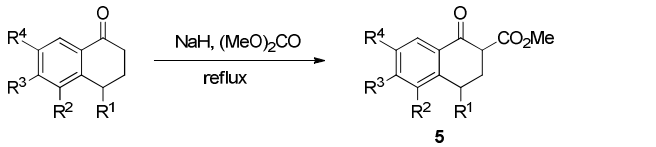
1-Hydroxy-2-naphthoates can be synthesized by: a) reaction of isocumarins with the Reformatsky reagent,[7] b) annulations of 2-formylbenzoate thioacetals with α,β-unsaturated esters followed by hydrolysis of the thioacetals with *N*-chlorosuccinimide or with mercury(II) perchlorate,[9] c) a three-component reaction of an aryne precursor, β-keto sulfones and α,β-unsaturated esters,[10] d) lithiation-carbonylation of α-methoxynaphthalenes,[6] e) condensation of phthalides with α,β-unsaturated esters,[8] and f) intramolecular cyclization of aryl substituted alkenyl β-keto esters by means of phenylselenyl chloride in the presence of $FeCl_3$[11] or by palladium.[12] Although, the most direct way for the preparation of these 1-hydroxy-2-naphthoates is the bromination-dehydrobromination of 2-substituted α-tetralones **5** bearing an ester group at the 2-position.[2,3,13] Alternatively, dehydrogenation reactions of compounds **5** using an excess of an α-iodoxybenzoic acid derivative[14] or 5% palladium on carbon in refluxing *p*-cymene[6] have been used. We communicate here the first catalyzed direct aromatization 2-(methoxycarbonyl)-α-tetralones (**5**) to methyl 1-hydroxy-2-naphthoates (**1**) under very simple and mild conditions using CuI or $Pd_2(dba)_3$ as catalysts.

2. Results and Discussion

During our studies on the arylation of 2-(methoxycarbonyl)-α-tetralone (**5a**) with 2-bromoanisol in the presence of copper salts, the so called Hurtley reaction,[15] we used the conditions recently described by Kwong *et al.*[16] for the arylation of 1,3-dicarbonyl compounds.[17] Interestingly, we found out that the use of CuI (5

mol%), picolinic acid (10 mol%) as ligand and Cs_2CO_3 as base in dioxane[16] at room temperature (30 ºC) for 2 d afforded exclusively MHNA (**1a**) instead of the corresponding α-arylated tetralone. At the same time, trying the Miura,[18] Buchwald[19] and Hartwig[20] palladium-catalyzed conditions, such as $Pd_2(dba)_3$ (2.5 mol%), K_3PO_4 as base in toluene at 70 ºC under Ar atmosphere, the same aromatization process was observed. These unexpected results prompted us to develop reaction conditions to the general synthesis of 1-hydroxy-2-naphthoates **1** from the corresponding 2-(methoxycarbonyl)-α-tetralones **5**.

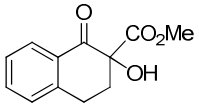
Firstly, the starting 2-(methoxycarbonyl)tetralones **5a**-**5h** were prepared by methoxycarbonylation of commercially available α-tetralones by means of dimethyl carbonate using 60% NaH as base under reflux in excellent yields (Scheme 1).[21]



5a: $R^1 = R^2 = R^3 = R^4 = H$ (92%)
5b: $R^1 = R^2 = R^3 = H$, $R^4 = OMe$ (87%)
5c: $R^1 = R^2 = R^4 = H$, $R^3 = OMe$ (98%)
5d: $R^1 = R^2 = H$, $R^3 = R^4 = OMe$ (97%)
5e: $R^1 = R^3 = R^4 = H$, $R^2 = OMe$ (96%)
5f: $R^1 = R^2 = R^3 = H$, $R^4 = F$ (93%)
5g: $R^1 = Me$, $R^2 = R^3 = R^4 = H$ (71%)
5h: $R^1 = R^3 = R^4 = H$, $R^2 = OBn$ (100%)

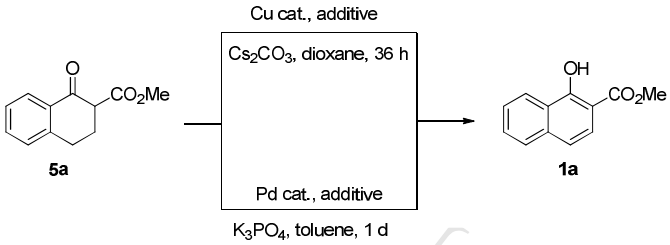
Scheme 1. Synthesis of keto esters **5.**

With the starting tetralones **5** in hand, they were submitted to the copper-catalyzed aromatization conditions (Table 1). In the case of tetralone **5a** the corresponding MHNA **1a** was obtained in 70% yield working with CuI (5 mol%), Cs_2CO_3 as base and picolinic acid (10 mol%) as additive under Ar atmosphere at 30 ºC during 48 h (Table 1, entry 1). This yield was increased to 85% using 10 mol% of CuI and 20 mol% of picolinic acid (Table 1, entry 2). In the absence of CuI the reaction gave **1a** in 32% yield (Table 1, entry 3). However, in the absence of picolinic acid, CuI was able to **catalyze** the aromatization of **5a** in 77% yield (Table 1, entry 4). When Cu nanoparticles (NPs) were used as catalyst only a 28% yield was observed (Table 1, entry 5). On the other hand, when this process was performed in the presence of air 87% yield was obtained (Table 1, entry 6). Increasing the temperature from 30 ºC to 70 ºC a higher 94% yield was achieved (Table 1, compare entries 6 and 7). Under MW irradiation at 70 ºC during 1 h only a 10% yield was achieved (Table 1, entry 8). When this reaction was performed in the absence of CuI, product **1a** was obtained in only 14% yield (Table 1, entry 9). On the other hand, when 1 eq. of CuI was used the formation of hydroxylated tetralone **6a**[22] in 61% yield was mainly observed (Table 1, entry 10). This type of hydroxylation of 1,3-dicarbonyls[23] has been observed in the case of malonates with cesium salts under air[24] and with CuOTf as catalyst (10 mol%) and oxaziridines as oxidants.[25]



6a

Table 1. Reaction conditions studies for the copper- and palladium-catalyzed aromatization of tetralones **5a** to methyl 1-hydroxynaphthoates **1a**.[a]



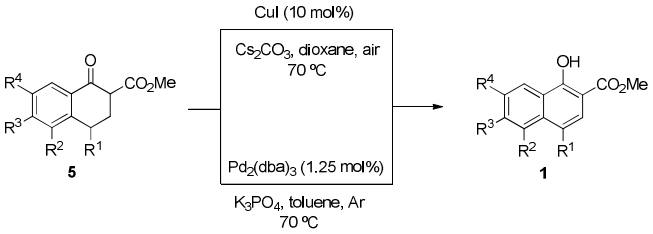
Entry	Cat (mol%)	Additive (mol%)	T (ºC)	Yield (%)[b]
1[c]	CuI (5)	Picolinic acid (10)	30	70
2[c]	CuI (10)	Picolinic acid (20)	30	85
3[c]	-	Picolinic acid (20)	30	32
4[c]	CuI (10)	-	30	77
5[c]	CuNPs (10)	-	30	28
6[d]	CuI (10)	-	30	87
7[d]	CuI (10)	-	70	94
8[d]	CuI (10)	-	70[e]	10
9[d]	-	-	70	14
10[d]	CuI (100)	-	70	5[f]
11	$Pd_2(dba)_3$ (1.25)	-	70	81
12	$Pd_2(dba)_3$ (1)	$Bu^t_3PHBF_4$ (4)	70	88
13	$Pd_2(dba)_3$ (0.5)	$Bu^t_3PHBF_4$ (4)	70	82
14	$Pd(OAc)_2$ (2.5)	$Bu^t_3PHBF_4$ (4)	70	80

[a] Cu-catalyzed conditions: **5** (0.2 mmol), Cu-cat (see column), additive (see column), Cs_2CO_3 (0.6 mmol), degassed 1,4-dioxane (3 mL) during 36 h ; Pd-catalyzed conditions: **5** (0.2 mmol), Pd-cat. (see column), K_3PO_4 (0.6 mmol), toluene (3 mL), argon atmosphere under 1 d.
[b] Isolated yield after chromatography.
[c] Under Ar.
[d] In the presence of air.
[e] Under MW irradiation at 150 W, 1 h.
[f] Compound **6a** was obtained 61 % yield.

When **5a** was treated with $Pd_2(dba)_3$ (1.25 mol%) and K_3PO_4 as base, **1a** was obtained in 81% yield after 24 h at 70 ºC in toluene under Ar atmosphere (Table 1, entry 11). The addition of $Bu^t_3PHBF_4$ (4 mol%) and 1 mol% of $Pd_2(dba)_3$ gave a slight higher 88% yield (Table 1, entry 12). Reducing to the half the Pd loading, naphthol **1a** was obtained in 82% yield (Table 1, entry 13). Finally, using $Pd(OAc)_2$ (2.5 mol%) and $Bu^t_3PHBF_4$ (4 mol%) a 80% yield was obtained (Table 1, entry 14). In order to work under phosphine-free conditions the first Pd-catalyzed conditions were chosen as the best method (Table 1, entry 11) to perform this aromatization process.

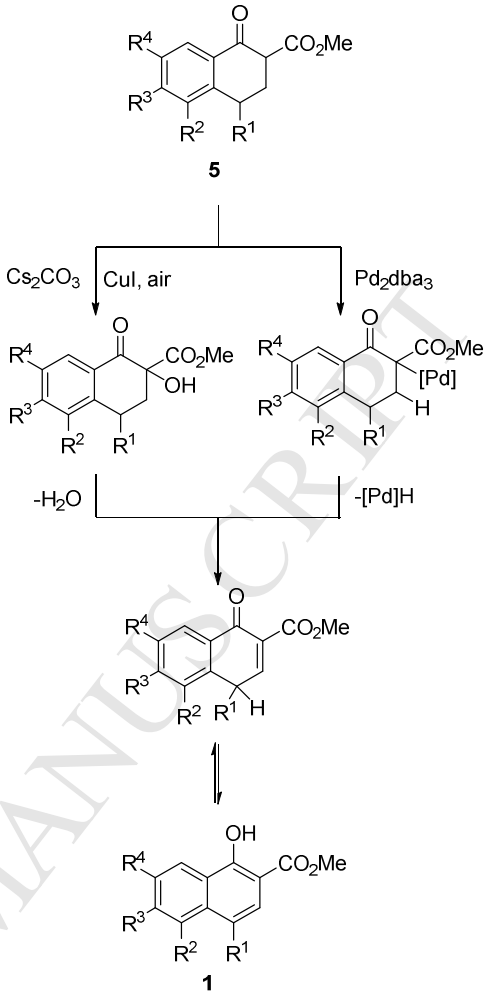
Parallel studies were considered during the scope studies of this aromatization process with different substituted α-tetralones

5 (Scheme 2 and Table 2). The synthesis of **1a** was carried out under the selected Cu- and Pd-catalyzed reaction conditions in 85% and 70 % yield, respectively (Table 2, entries 1 and 2). In the case of 7-methoxy substituted α-tetralone **5b** naphthoate **1b** was obtained in a higher 94% yield under CuI catalyzed conditions (Table 2, entry 3). However, by using $Pd_2(dba)_3$ (1 mol%) the addition of $Bu^t_3PHBF_4$ (4 mol%) was necessary to achieve a 40% yield (Table 2, entry 4). Naphthoate **1c**, with a methoxy group at the 5-position was also obtained in higher yield when CuI was used as catalyst (89% *versus* 70%, Table 2, entries 5 and 6). The aromatization of the 6,7-dimethoxy substituted α-tetralone **5d** only worked with CuI giving **1d** in 47% yield (Table 2, entries 7 and 8). Monomethoxylated α-tetralone **5e** gave the 5-methoxynaphthoate **1e** in 87% and 69% yield, respectively (Table 2, entries 9 and 10). The α-tetralone **5f** with a fluorine substituent at the 7-position gave product **1f** in 77% and 53% yield, respectively (Table 2, entries 11 and 12). Lower yields (57% and 35%) were observed in the case of the 4-methyl substituted α-tetralone **5g** (Table 2, entries 13 and 14). Finally, the 6-benzyloxytetralone **5h** gave product **1h** in very good yields under both reaction conditions (97% and 83%, Table 2, entries 15 and 16).



Scheme 2. Syntheis of methyl 1-hydroxy-2-naphthoates **1** by aromatization of α-tetralones **5**.

A possible mechanism for the copper-catalyzed process could be the formation of the α-hydroxylated 2-(methoxycarbonyl)-α-tetralone followed by dehydration to the unsaturated α-tetralone and enolization to the naphthoate. This proposal is based on the described methodologies above mentioned, the α-hydroxylation of acyclic 1,3-dicarbonyl compounds by means of cesium salts in DMF[24] and the Cu-catalyzed oxidation with oxaziridines.[25] On the other hand, aromatization processes from α-hydroxy tetralones by dehydration have been described.[26] However, in the case of the Pd-catalyzed aromatization, the first α-hydroxylation step was discharged because the Pd-catalyzed reaction was performed under Ar atmosphere. Most of the described Pd-catalyzed α-hydroxylation methodologies are performed in the presence of air or other oxidants.[27] We have proposed the initial formation of the *O*-palladium enolate in equilibrium with the *C*-palladium enolate, which evolves by β-hydride elimination to the same unsaturated α-tetralone. In fact, aromatization processes of cyclohexanones and cyclohexenones catalyzed by $CuCl_2$,[28] iodine,[29] vanadium oxides[30] or Pd[31,32] have been described. Final 1,6-tautomerization of this unsaturated α-tetralone would provide the corresponding naphthol.

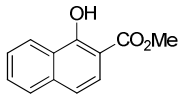
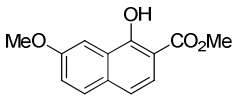
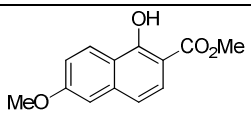
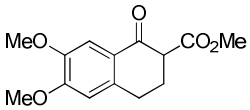
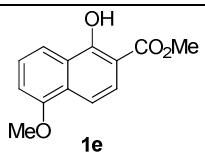
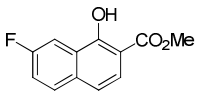
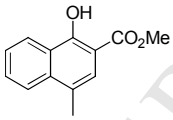
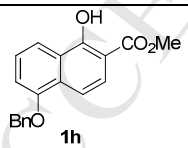


Scheme 3. Proposed mechanisms for the aromatization processes.

3. Conclusions

The aromatization of tetralones **5** to 1-hydroxy-2-naphthoates **1** occurs under copper-catalyzed conditions in high conversions at 70 °C, in spite of the substituent at the aromatic ring. In contrast, the palladium-catalyzed reaction conditions showed to be very sensitive to substituent effects. The aromatization of 2-(methoxycarbonyl)-α-tetralones with CuI is less expensive and can be performed in the presence of air, leading to the corresponding methyl 1-hydroxy-2-naphthoates in better yields and shorter reaction time.

Table 2. Copper- and palladium-catalyzed aromatization of α-tetralones **5** to methyl 1-hydroxynaphthoates **1**.[a]

Entry	1	Catalyst	Time (h)	Conversion[b]	Yield (%)[c]
1	 **1a**	CuI	36	100	94
2		$Pd_2(dba)_3$	24	95	81
3	 **1b**	CuI	36	99	94
4		$Pd_2(dba)_3$[d]	210	40	40
5	 **1c**	CuI	36	100	89
6		$Pd_2(dba)_3$[e]	48	100	70
7	 **1d**	CuI	36	55	47
8		$Pd_2(dba)_3$	120	-	-
9	 **1e**	CuI	36	100	87
10		$Pd_2(dba)_3$[e]	120	74	69
11	 **1f**	CuI	36	100	77
12		$Pd_2(dba)_3$	120	55	53
13	 **1g**	CuI	36	64	57
14		$Pd_2(dba)_3$	48	43	35
15	 **1h**	CuI	36	100	97
16		$Pd_2(dba)_3$	48	80	83

[a] Cu-catalyzed conditions: **5** (0.2 mmol), CuI (10 mol%), Cs_2CO_3 (0.6 mmol), degassed 1,4-dioxane (3 mL), air at 70 ºC; Pd-catalyzed conditions: **5** (0.2 mmol), $Pd_2(dba)_3$ (1.25 mol%), K_3PO_4 (0.6 mmol), toluene (3 mL), 70 ºC, argon atmosphere .
[b] Determined by ^1H NMR (300 MHz).
[c] Isolated yields after chromatography.
[d] $Pd_2(dba)_3$ (1 mol%) and *t*-Bu_3PHBF_4 (4 mol%) were used.
[e] 1 mol% of $Pd_2(dba)_3$ was used.

4. Experimental section

4.1. General

Melting points were determined on a Fisatom 430 apparatus. ^1H NMR and ^{13}C NMR spectra were obtained using a Varian Gemini-200 (400 and 500 MHz) with $CDCl_3$ as solvent and TMS as internal standard. IR spectra were recorded on a Nicolet 510 P-FT. Low resolution's mass spectra were obtained at 70 eV by electron impact in a unit for direct insertion, MS Micromass MM12F. Analytical TLC was performed on Merck aluminum sheets with silica gel 60

F_{254}. For flash chromatography, Merck silica gel 60 (0.040–0.063 mm) was employed.

4.2. Typical procedure for the synthesis of 2-(methoxycarbonyl)tetralones 5.

A solution of α-tetralone (10 mmol) in dimethyl carbonate (5 mL) was added to a stirred suspension of NaH (60% dispersion, 15 mmol) in dimethyl carbonate (10 mL) under argon atmosphere. The solution was refluxed and once the reaction was judged complete after a TLC test the solvent was evaporated. The resultant solid was dissolved in hydrochloric acid (2 M) and the phases were separated. The aqueous phase was extracted with ethyl acetate (3 x 15 mL). The organic extracts were dried ($MgSO_4$) and evaporated to dryness. Flash chromatography (EtOAc/hexane 10%) afforded the pure products.

*Methyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**5a**).*[33] Yield 92%; brown solid; mp = 66-68 °C; R_f 0.35 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 2946; 2897; 1728; 1677; 1598; 1451; 1372; 1313; 1156; 949; 900; 732; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 12.41 (s, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.47-7.43 (m, 1H), 7.30-7.23 (m, 3H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.1 Hz), 3.79 (s, 3H), 3.75 (s, 3H), 3.59 (dd, *J* = 10.5, 4.7 Hz, 1H), 3.04-2.92 (m, 2H), 2.77 (dd, *J* = 10.8, 4.6 Hz, 2H), 2.57-2.51 (m, 2H), 2.49-2.42 (m, 1H), 2.34-2.29 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 193.3, 173.2, 170.7, 165.2, 143.8, 139.5, 134.0, 131.8, 130.6, 130.0, 128.9, 127.8, 127.5, 127.0, 126.7, 124.4, 96.9, 54.5, 52.5, 51.8, 27.8, 27.7, 26.5, 20.6; MS (EI) *m/z* (%): 204 (M^+), 189, 172, 144, 127, 118, 115, 90, 77, 63, 51.

*Methyl 7-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**5b**).*[34] Yield 87%; brown oil; R_f 0.32 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 2995, 2946, 2838, 1746, 1677, 1647, 1598, 1569, 1441, 1322, 1264, 1273, 1224, 880, 811, 702; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 12.44 (s, 1H), 7.50 (d, *J* = 2.8 Hz, 1H), 7.33 (d, *J* = 2.7 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.06 (dd, *J* = 8.4, 2.9 Hz, 2H), 6.87 (dd, *J* = 8.3, 2.7 Hz, 1H)., 3.81 (s, 6H), 3.78 (s, 3H), 3.77 (s, 3H), 3.59 (dd, *J* = 10.3, 4.7 Hz, 1H), 3.02 – 2.85 (m, 2H), 2.72 (t, *J* = 7.7 Hz, 1H), 2.53 (dd, *J* = 8.7, 6.7 Hz, 1H), 2.46 (ddd, *J* = 15.1, 9.4, 4.6 Hz, 1H), 2.37 – 2.28 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 193.51, 173.18, 170.78, 165.13, 156.76, 155.93, 132.76, 131.05, 127.75, 127.15, 126.90, 119.24, 116.81, 114.71, 112.79, 96.80, 55.74, 55.67, 54.13, 52.34, 51.69, 25.65, 21.29, 20.03; MS (EI) *m/z* (%): 234 (M^+), 216, 202, 174, 160, 148, 131, 120, 103, 91, 77, 63, 51.

*Methyl 6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**5c**).*[14] Yield 98%; brown solid; mp = 78-80 °C; R_f 0.10 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 2957, 2838, 1720, 1668, 1600, 1254, 1214, 1156, 998, 840, 664; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 12.47 (s, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 6.81 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.77 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.69-6.67 (m, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.76, (s, 3H), 3.56 (dd, *J* = 10.3, 4.7 Hz, 1H), 3.07 – 2.88 (m, 2H), 2.79 – 2.73 (m, 2H), 2.54 (dd, *J* = 8.8, 6.6 Hz, 2H), 2.51 – 2.40 (m, 1H), 2.31 (ddd, *J* = 13.4, 10.5, 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 191.9, 173.2, 170.9, 165.6, 164.1, 161.6, 146.3, 141.9, 130.4, 126.3, 125.4, 122.9, 113.3, 112.7, 111.8, 94.9, 55.6, 55.4, 54.3, 52.4, 51.6, 28.3, 28.1, 26.6, 20.7; MS (EI) *m/z* (%): 234 (M^+), 202, 174, 160, 148, 131, 120, 103, 91, 77, 63, 51.

*Methyl 6,7-dimethoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**5d**).*[35] Yield 97%; brown solid; mp = 126-128 °C; R_f 0.04 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 2937, 2830, 1736, 1657, 1509, 1451, 1372, 1273, 1135, 1027; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 12.56 (s, 1H), 7.52 (d, *J* = 1.8 Hz, 1H), 7.33 (s, 1H), 6.69 (s, 1H), 6.67 (d, *J* = 5.6 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.92 (s, 3H), 3.91 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H), 3.58 (dd, *J* = 9.8, 4.8 Hz, 1H), 3.05 – 3.00 (m, 1H), 3.00 – 2.88 (m, 9H), 2.79 – 2.71 (m, 1H), 2.60 (dd, *J* = 11.8, 4.9 Hz, 2H), 2.57 – 2.44 (m, 5H), 2.34 (ddt, *J* = 13.4, 6.2, 4.7 Hz, 4H), 2.17 – 2.08 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 191.9, 173.2, 170.9, 165.5, 154.0, 150.9, 148.2, 138.8, 133.3, 124.8, 122.4, 110.5, 110.2, 108.9, 107.3, 94.8, 56.1, 56.0, 53.8, 52.3, 51.6, 27.5, 27.4, 26.8, 20.7; MS (EI) *m/z* (%): 264 (M^+), 206, 191, 178, 164, 150, 135, 107, 91, 77, 63, 51.

*Methyl 5-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**5e**).*[36] Yield 96%; brown solid; mp = 60-62 °C; R_f 0.32 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 2957, 2897, 1726, 1687, 1579, 1362, 1441, 1254, 1205, 1146, 900, 801, 781; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 12.40 (s, 1H), 7.63 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.01 (dd, *J* = 8.1, 0.6 Hz, 1H), 6.95 – 6.89 (m, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H), 3.76 (s, 3H), 3.58 (dd, *J* = 10.7, 4.7 Hz, 1H), 3.07 (dt, *J* = 17.9, 5.1 Hz, 1H), 2.77 (ddd, *J* = 14.4, 8.6, 3.8 Hz, 3H), 2.52 (dd, *J* = 8.6, 7.3 Hz, 2H), 2.43 (tdd, *J* = 10.5, 7.8, 4.9 Hz, 1H), 2.37 – 2.28 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 193.6, 173.2, 170.8, 165.1, 156.8, 155.9, 132.8, 131.1, 127.8, 127.2, 126.9, 119.3, 116.8, 114.7, 112.8, 96.8, 55.8, 55.7, 54.2, 52.4, 51.7, 25.7, 21.3, 20.1, 20.0; MS (EI) *m/z* (%): 234 (M^+), 234, 202, 174, 159, 148, 131, 120, 103, 90, 77, 63, 51.

*Methyl 7-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**5f**).*[37] Yield 93%; brown solid; mp = 55-57 °C; R_f 0.22 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 3082, 3024, 2937, 1648, 1629, 1570, 1433, 1326, 1219, 1200, 1014, 800, 720; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 12.34 (s, 1H), 7.69 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.47 (dd, *J* = 9.5, 2.7 Hz, 1H), 7.27 – 7.17 (m, 2H), 7.12 (dd, *J* = 8.3, 5.4 Hz, 1H), 7.00 (td, *J* = 8.4, 2.7 Hz, 1H), 3.83 (s, 1H), 3.78 (s, 1H), 3.61 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.09 – 2.90 (m, 2H), 2.77 (t, *J* = 7.8 Hz, 2H), 2.56 (dd, *J* = 8.8, 6.7 Hz, 2H), 2.53 – 2.44 (m, 1H), 2.41 – 2.32 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 192.2, 172.9, 170.4, 163.9, 162.9 (d, *J* = 12.0 Hz), 160.5 (d, *J* = 14.8 Hz), 139.5 (d, J=1.5), 134.9 (d, *J* = 2.4 Hz), 133.3 (d, *J* = 6.3 Hz), 131.7 (d, *J* = 6.3 Hz), 130.8 (d, J=6.0Hz), 128.8 (d, *J* = 7.6 Hz), 121.4 (d, *J* = 22.3 Hz), 117.1 (d, J=15.8), 113.6 (d, J=16.5), 111.4 (d, *J* = 15.9 Hz), 97.8, 54.1, 52.5, 51.8, 27.0, 26.9, 26.5, 20.7; MS (EI) *m/z* (%): 222 (M^+), 207, 190, 162, 145, 133, 115, 108, 90, 63, 57.

*Methyl 4-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**5g**).*[38] Yield 71%; brown solid; mp = 65-67 °C; R_f 0.45 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 2957, 2848, 1715, 1647, 1618, 1559, 1441, 1352, 1264, 811, 772; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 12.37 (s, 1H), 8.04 (t, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.54 (dt, *J* = 14.6, 7.4 Hz, 1H), 7.40 (dd, *J* = 7.1, 4.5 Hz, 1H), 7.35 (dd, *J* = 6.5, 5.6 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.26 (d, *J* = 3.4 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 3.82 (s, 1H), 3.81 (s, 1H), 3.66 (dd, *J* = 13.5, 4.6 Hz, 1H), 2.97 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.71 (d, *J* = 6.2 Hz, 1H), 2.67 (d, *J* = 6.2 Hz, 1H), 2.39 (dd, *J* = 15.6, 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 193.4, 193.1, 173.3, 170.9, 170.8, 164.6, 148.4, 147.7, 144.3, 134.2, 130.9, 129.1, 128.3, 128.1, 127.9, 127.8, 126.9, 126.8, 126.6, 126.1, 124.6, 95.4, 55.1, 52.4, 52.3, 51.7, 50.9, 35.0, 33.2, 31.9, 31.0, 28.3, 21.3, 20.3, 20.2; MS

(EI) *m/z* (%): 218 (M^+), 203, 187, 171, 158, 144, 131, 115, 104, 91, 77, 63, 51.

*Methyl 5-(benzyloxy)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**5h**).* From 5-(benzyloxy)-3,4-dihydronaphthalen-1(2H)-one (7).[39] Yield 100%; brown solid; mp = 72 °C; R_f 0.35 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 2951, 2924, 2869, 2851, 1738, 1679, 1573, 1460, 1257, 1204, 993, 751, 700; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 12.41 (s, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.32 (m, 10H), 7.24 (dt, *J* = 16.5, 8.0 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 5.09 (s, 2H), 5.07 (s, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 3.60 (dd, *J* = 10.6, 4.7 Hz, 1H), 3.15 (dt, *J* = 17.9, 5.2 Hz, 1H), 2.89 (d, *J* = 7.2 Hz, 1H), 2.84 (dd, *J* = 11.0, 6.7 Hz, 2H), 2.56 – 2.50 (m, 1H), 2.45 (ddd, *J* = 14.4, 9.2, 4.4 Hz, 1H), 2.38 – 2.30 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 193.5, 173.2, 170.8, 165.1, 155.9, 155.1, 137.1, 136.7, 133.1, 132.9, 131.2, 128.73, 128.66, 128.3, 128.2, 128.1, 127.3, 127.2, 126.9, 119.6, 117.2, 116.2, 114.4, 96.9, 70.42, 70.38, 54.1, 52.45, 52.38, 51.78, 51.71, 29.8, 25.6, 21.5, 20.3, 19.9; HRMS calcd for $C_{19}H_{18}O_4$ 310.1205 found 310.1198.

4.3. General procedure for direct aromatization reaction under Cu catalysis.

To a mixture of tetralone **5** (0.2 mmol), CuI (4 mg, 10 mol%), Cs_2CO_3 (195mg, 0.6 mmol) was added degassed 1,4-dioxane (3 mL) and the mixture was stirred at 70 ºC under air for the time indicate in Table 2. Then water was added (10 mL) and the reaction was extracted with ethyl acetate (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, and evaporated under vacuum. The pure compounds were obtained after flash or preparative chromatography.

4.4. General procedure for direct aromatization reaction under Pd catalysis.

To a mixture of tetralone **5** (0.2 mmol), $Pd_2(dba)_3$ (5 mg, 1.25 mol%), K_3PO_4 (127 mg, 0.6 mmol) was added toluene (3 mL) and the mixture was stirred at 70 ºC under argon for the time indicate in Table 2. Then brine was added (10 mL) and the reaction was extracted with ethyl acetate (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, and evaporated under vacuum. The pure compounds were obtained after flash or preparative chromatography.

*Methyl 1-hydroxy-2-naphthoate (**1a**).*[40] Yield 94%; brown-yellow solid; mp = 44-46 °C; R_f 0.70 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 3055, 2946, 2848, 1688, 1638, 1569, 1431, 1343, 1196, 1086, 988, 762; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H: 11.99 (s, 1H), 8.40 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.64 – 7.56 (m, 1H), 7.51 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.26 (d, *J* = 8.9 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C: 171.5, 160.8, 137.3, 129.5, 127.6, 125.9, 124.8, 124.3, 123.9, 118.7, 105.7, 52.4; MS (EI) *m/z* (%): 202 (M^+), 170, 142, 114, 101, 88, 71, 63, 51.

*Methyl 1-hydroxy-7-methoxy-2-naphthoate (**1b**).*[12] Yield 94%; yellow oil; R_f 0.51 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 1663, 1619, 1425, 1340, 1247, 802, 783; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 11.94 (s, 1H), 7.71 – 7.62 (m, 3H), 7.29 – 7.21 (m, 2H), 4.0 (s, 3H), 3.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 171.7, 159.8, 157.8, 132.6, 129.1, 125.7, 122.1, 121.9, 118.5, 106.1, 101.9, 55.6, 52.4; MS (EI) *m/z* (%): 232 (M^+), 200, 157, 144, 130, 100.

*Methyl 1-hydroxy-6-methoxy-2-naphthoate (**1c**).*[14] Yield 89%; White Solid; mp = 103-105 °C; R_f 0.59 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 1660, 1609, 1444, 119; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H (ppm) 11.95 (s, 1H), 8.31 (d, *J* = 9.2 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.19 – 7.12 (m, 2H), 7.06 (d, *J* = 2.4 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C (ppm) 171.6, 161.1, 160.6, 139.3, 125.8, 125.3, 119.6, 117.9, 117.7, 106.2, 104.2, 55.5, 52.3; MS (EI, 70 eV): *m/z* (%): 232 (M^+), 201, 173, 59, 31.

*Methyl 1-hydroxy-6,7-dimethoxy-2-naphthoate (**1d**).*[41] Yield 47%; white solid; mp = 144-145 °C; R_f 0.23 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 3000, 2982, 2918, 2850, 1655, 1609, 1587, 1421, 1348, 1262, 1206, 1163, 1083, 974, 742; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 11.91 (s, 1H), 7.70 – 7.63 (m, 2H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.07 (s, 1H), 4.04 (s, 1H), 4.02 (s, 1H), 3.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 171.7, 159.6, 152.1, 149.3, 133.8, 123.1, 119.5, 117.4, 106.4, 104.7, 102.6, 56.2, 56.1, 52.3; MS (EI) *m/z* (%): 262 (M^+), 231, 203, 59, 31.

*Methyl 1-hydroxy-5-methoxy-2-naphthoate (**1e**).*[42] Yield 87%; yellow solid; mp = 112-114 °C; R_f 0.54 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 2995, 2966, 2888, 1668, 1598, 1441, 1254, 1156, 1057, 946; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 11.91 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 9.1 Hz, 1H), 7.69 (d, *J* = 9.1 Hz, 1H), 7.44 (t, *J* = 8.1 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 4.00 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 171.5, 160.5, 155.1, 129.1, 125.9, 123.6, 115.8, 112.7, 107.6, 106.2, 55.7, 52.3; MS (EI) *m/z* (%): 232 (M^+), 200, 185, 157, 144, 129, 115, 101, 89, 75, 63, 51.

*Methyl 7-fluoro-1-hydroxy-2-naphthoate (**1f**).*[12] Yield 77%; white solid; mp = 85-87 °C; R_f 0.62 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 3084, 2946, 2927, 2848, 1657, 1598, 1509, 1441, 1383, 1244, 1156, 1077, 1008, 811, 752, 743; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 11.92 (s, 1H), 8.01 (dd, *J* = 10.0, 2.4 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.37 (td, *J* = 8.6, 2.6 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 171.4, 162.4, 160.2 (d, *J* = 5.0 Hz), 159.1, 134.1, 129.9 (d, *J* = 8.5 Hz), 125.8 (d, *J* = 8.9 Hz), 123.6 (d, *J* = 2.3 Hz), 119.5 (d, *J* = 25.1 Hz), 118.5, 108.0 (d, *J* = 22.5 Hz), 106.4, 52.6; MS (EI) *m/z* (%): 220 (M^+), 207, 188, 164, 132, 108, 94, 81, 74, 63, 51.

*Methyl 1-hydroxy-4-methyl-2-naphthoate (**1g**).*[41] Yield 57%; white solid; mp = 92-94 °C; R_f 0.70 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 3058, 2955, 2919, 2850, 1659, 1634, 1445, 1344, 1243, 1157, 1092, 1001, 799, 762; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 11.80 (s, 1H), 8.45 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.66 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.60 (d, *J* = 0.8 Hz, 1H), 7.54 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 4.00 (s, 3H), 2.57 (d, *J* = 0.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 171.6, 159.7, 136.5, 129.4, 125.6, 125.0, 124.6, 124.5, 124.2, 123.9, 105.1, 52.4, 18.9; MS (EI) *m/z* (%): 242 (M^+Na), 216 (M^+).

*Methyl 5-(benzyloxy)-1-hydroxy-2-naphthoate (**1h**).* Yield 97%; brown solid; mp = 129-132 °C; R_f 0.55 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 3063, 2998, 2948, 2923, 2868, 2850, 1651, 1599, 1450, 1343, 1250, 1149, 1046, 761, 709; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 11.93 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.36 (dd, *J* = 8.6, 6.0 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 5.24 (s, 2H), 4.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 171.6, 160.6, 154.3, 136.9, 129.4, 128.8, 128.2, 127.5, 125.98, 125.96, 123.7, 116.2, 113.0, 109.1, 106.3, 70.4, 52.4; HRMS calcd for $C_{19}H_{16}O_4$ 308.1049, found 308.1046.

*Methyl 2-hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**6a**).*[22] In this case 1 equiv of CuI was used. Yield 61%; brown pale solid; mp = 67-69 °C; R_f 0.09 (hexane/EtOAc 10/1). IR (KBr) (cm^{-1}): 3462, 1745, 1677, 1272; ^{1}H NMR (400 MHz, $CDCl_3$)

δ_H: 8.06 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.54 (td, *J* = 7.6, 1.3 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 6.7 Hz, 1H), 4.34 (s, 1H), 3.75 (s, 3H), 3.16 – 3.10 (m, 2H), 2.73 (dt, *J* = 13.5, 5.0 Hz, 1H), 2.26 (ddd, *J* = 13.6, 9.1, 6.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 194.7, 171.2, 144.2, 134.6, 130.2, 129.1, 128.4, 127.1, 53.2, 32.8, 25.7; MS (EI) *m/z* (%): 220 (M^+), 203, 161, 59, 17.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/...

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